Electroresponsive Polymers

Helical, Chiral Polyisocyanides Bearing Ferrocenyl Groups as Pendants: Synthesis and Properties**

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Recent developments in polymer synthesis have provided us with new methods for preparing nano-sized polymer molecules with precisely controlled chemical sequence, molecular weight, and stereostructure, as well as molecular shape.[1]

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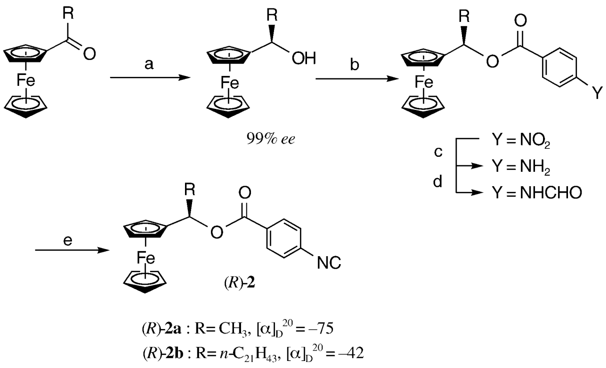
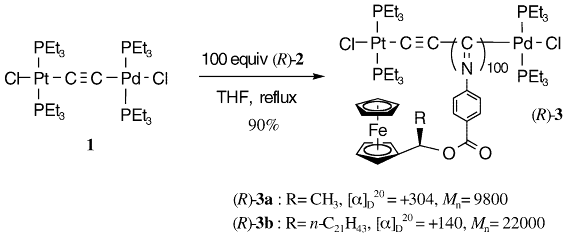
Nano-sized metal-containing polymers are promising candidates as single-molecular devices.[2] Ferrocene is a redox-active organometallic compound and exists in two stable oxidation states of Fe^{II} (neutral ferrocene) and Fe^{III} (ferrocenium cation) which are interconvertible by oxidation and reduction. Several ferrocene-containing polymers including dendrimers have already been prepared as potential functional materials.[3] Polyisocyanides consist of an sp^2-hybridized carbon main chain and imino side groups, and have been attracting much attention in terms of their unique helical structure.[4] We have reported a living polymerization system for isocyanides with a dinuclear Pt–Pd complex initiator **1**[5] and the synthesis of novel polyisocyanides bearing chiral pendants which predominantly form one-handed helical structures in solution.[6] Now we have successfully synthesized helical, chiral, ferrocene-containing polyisocyanide compounds which exhibit a sharp response with a reversible conformational change on electrical stimulus.

Known responsive polymers, such as polyisocyanates,[7] polypeptides,[8] polymethacrylates,[9] polysilanes[10] and polyacetylenes,[11] are sensitive to light irradiation, thermal treatment, and chemical interaction, whereas there are no responsive polymers to date whose conformation can be controlled by electrical stimuli. Helical, chiral poly(ferrocenyl polyisocyanide)s may be prepared by the polymerization of chiral ferrocenyl isocyanides with initiator **1**. Thus, chiral isocyanides **2** which contain ferrocenyl groups were synthesized in 99% *ee* from acylferrocene by an asymmetric reaction (Scheme 1).[12,13] We can prepare polymers with various polymerization degrees from **2** by exploiting the living nature of the polymerization. Treatment of 100 equivalents (*R*)-**2a** with **1** in refluxing THF for 20 h gave polyisocyanide (*R*)-**3a** with $M_n = 9800$ and a narrow polydispersity index (PDI) = 1.15 in 93% yield (Scheme 2). Thus prepared polymer (*R*)-**3a** showed a specific rotation of +304, although the specific rotation of (*R*)-**2a** was −75. Polymer (*S*)-**3a** prepared from (*S*)-**2a** ($[\alpha] = +77$) showed a specific rotation of −300. The large values of specific rotation of polymers **3a** with the opposite sign to those of monomers **2a** suggests that the polymers adopt predominantly a one-handed helical structure in a solution.[6] The CD spectra of (*R*)-**3a** exhibited a strong positive Cotton effect at 360 nm and a strong negative one at 250 nm, the former is assigned to the n–π* transition of the imino chromophores and the latter to the π–π* transition of the benzene rings. The positive Cotton effect at 360 nm suggests the right-handed helical structure of polymer (*R*)-**3a**, in contrast (*S*)-**3a** showed a strong negative Cotton effect at 360 nm indicating a polymer main chain with a left-handed helix structure.[14]



(*R*)-**2a** : R = CH_3, $[\alpha]_D^{20} = -75$
(*R*)-**2b** : R = *n*-$C_{21}H_{43}$, $[\alpha]_D^{20} = -42$

Scheme 1. Synthesis of chiral isocyanides **2**. a) Cat*, BH_3, 79%; b) *p*-nitrobenzoyl chloride, pyridine, 77%; c) H_2, Pd/C, 99%; d) HCO_2H, DCC, 75%; e) $POCl_3$, $NH(iPr)_2$, 81%. Cat* = (*S*)-2-methyl-CBS-oxazaborolidine, DCC = *N*,*N*'-dicyclohexylcarbodiimide.



(*R*)-**3a** : R = CH_3, $[\alpha]_D^{20} = +304$, $M_n = 9800$
(*R*)-**3b** : R = *n*-$C_{21}H_{43}$, $[\alpha]_D^{20} = +140$, $M_n = 22000$

Scheme 2. Synthesis of polyisocyanides **3** bearing chiral ferrocenyl groups as pendants.

The electrochemical properties of polymer (*R*)-**3a** were investigated by cyclic voltammetry (CV). Polymer (*R*)-**3a** showed reversible oxidation and reduction with a half-wave potential of approximately 0.6 V (vs Ag/AgCl), however, gave a small peak/current ratio $|i_{p,a}/i_{p,c}|$ of 0.63. This waveform suggested deposition of the oxidized polymer onto the electrode as often seen for some ferrocene-containing compounds[15] as a result of the low solubility of the cationic polymers.

To improve the solubility of polymers, a long alkyl substituent (C_nH_{2n+1}: $n = 7$, 11, and 21) was introduced at the chiral carbon atom of monomer **2a**. Thus, (*R*)-**2b** ($[\alpha] = -42$) having a $C_{21}H_{43}$ was synthesized with 99% *ee* (Scheme 1) and polymerized with initiator **1** ((*R*)-**2b**/**1** molar ratio = 100) to give polymer (*R*)-**3b** with $M_n = 22000$ and PDI = 1.15 in 90% yield (Scheme 2). The specific rotation and CD spectrum indicated a right-handed helical structure[14] of (*R*)-**3b** (Figure 1). The cyclic voltammogram of the polymer in CH_2Cl_2 (Figure 2) showed a reversible oxidation and reduction behavior, and the same half-wave

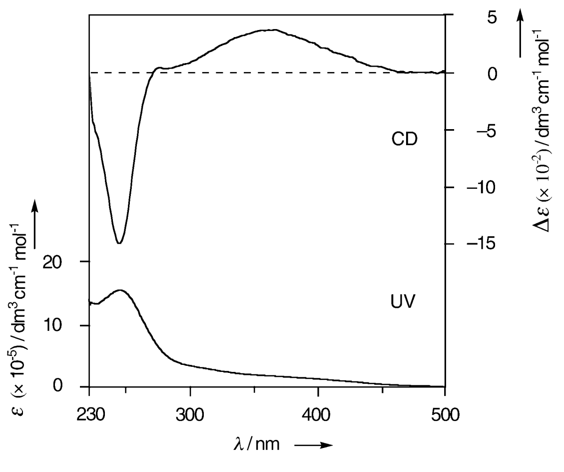


Figure 1. CD (Top) and UV (bottom) spectra of (*R*)-**3b**.

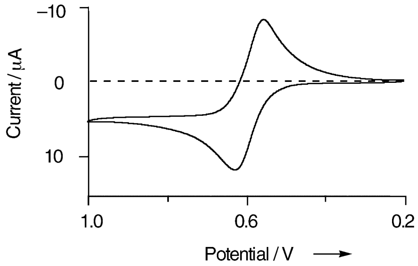


Figure 2. Cyclic voltammogram of (*R*)-**3b**. Recorded with $[NBu_4][PF_6]$ as electrolyte in CH_2Cl_2 (0.1 mol L^{-1}) at ambient temperature with a scan rate of 0.05 V s^{-1}. Potentials are expressed versus Ag/AgCl.

potential of approximately 0.6 V as polymer (*R*)-**3a**. However, in comparison with **3a** polymer **3b** gave a higher peak/current ratio $|i_{p,a}/i_{p,c}|$ of 0.92 and no deposition on the electrode was observed, which indicates that the long alkyl group improved the solubility of the oxidized polymer, as expected. We performed three cycles of redox and observed no appreciable changes in the voltammograms, which indicates that the redox process is completely reversible.

To investigate the response of (*R*)-**3b** towards an electrical stimulus, electrolytic CD and UV spectra were measured.[16] When polymer (*R*)-**3b**, dissolved in CH_2Cl_2, was electrochemically oxidized at 1.0 V, the CD spectrum clearly showed that the intensity of the positive Cotton effect at 360 nm decreased to around 40 % of that before oxidation and the negative Cotton effect at 250 nm almost disappeared (Figure 3). The same change in intensity of the Cotton effects was observed on oxidation at a higher applied potential of 1.5 V. In the UV spectrum new broad absorption bands appeared at 240–310 (Figure 3) and at 620 nm (not shown), which are assigned to a ferrocenium chromophore.[17] Subsequent electrolytic reduction of the ferrocenium cation at 0.2 V led to an increase in intensity of the Cotton effects and to recovery to the original intensity. The intensity change of both Cotton effects at 250 and 360 nm was repeated on further electrolytic oxidation and reduction. Since any changes of the UV spectra except the absorption resulting from the ferrocenium chromophore were not observed, the dramatic CD change suggests reversible conformational transformation of the helical main chain by an electrical stimulus.

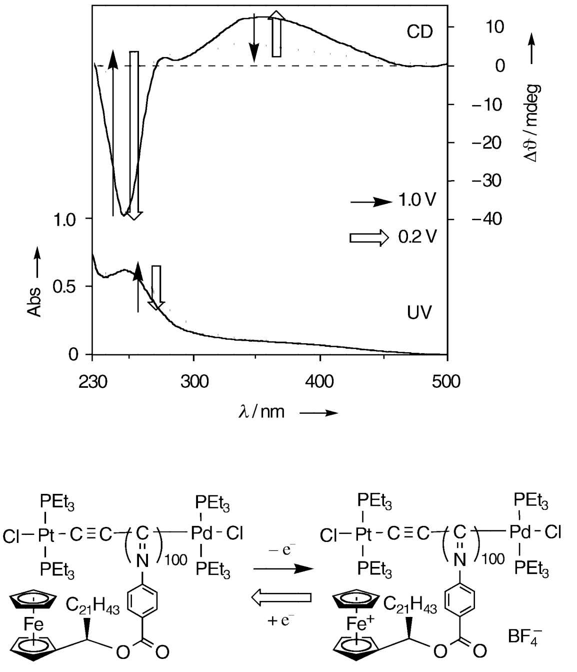


Figure 3. Electrolytic CD (top) and UV (bottom) spectra of the oxidation/reduction of (*R*)-**3b**.

On the other hand, on application of the same electrode potential (1.0 V) to a polyisocyanide compound bearing redox-inactive (*l*)-menthyl pendants,[6b] which has a right-handed helix, no changes were observed in the electrolytic CD and UV spectra, which indicates that the conformational structure of polyisocyanide chains was not affected directly by electrical stimuli.

We tried controlling the helical structure of the main chain not only by electrolytic redox but also by chemical oxidation and reduction of ferrocenyl groups[3a] in (*R*)-**3b**. On oxidation of the polymer with $[NO][PF_6]$ in CH_2Cl_2 the intensity of the Cotton effect at 360 nm decreased to about 40 % of that before oxidation, and the Cotton effect at 250 nm almost disappeared. UV absorption bands assigned to a ferrocenium cation appeared at 240–310 and 620 nm. Then, the reduction of ferrocenium groups with $[Cp^*_2Fe]$ (Cp^* = pentamethylcyclopentadienyl) recovered the initial intensities of the Cotton effects at 250 and 360 nm. These phenomena are the same as those observed for electrolytic oxidation and reduction, and undoubtedly reveal a driving force for the conformational transformation of helical polymers **3** to be electrostatic repulsion between the ferrocenium cations in the side chains generated by oxidation. Decrease of the Cotton effect intensities at 250 and 360 nm after oxidation suggests that electrostatic repulsion among the ferrocenium cations caused dislocation of the imino groups and benzene rings to positions which disturb the regular helical conformation of the polymer. In other words, the main chains of **3** are transformed from a helical structure to a disordered one, naturally resulting in loss of helical chirality.

In conclusion, we synthesized novel helical, chiral polyisocyanides **3** bearing ferrocenyl pendants which exhibit response towards oxidation and reduction with conformational change.

Experimental Section

Pt–Pd dinuclear complex **1** was prepared by the method reported in ref. [5a].

(*R*)-**3a**: A solution of complex **1** (3.0 mg, 3.5 µmol) in THF (10 mL) was added to (*R*)-**2a** (126 mg, 0.35 mmol). The mixture was stirred for 20 h under reflux. After the solution was concentrated to about 1 mL, it was poured into methanol (100 mL). The precipitate was collected by filtration and washed with methanol to give (*R*)-**3a** as a yellow solid (120 mg, 93 %). $[\alpha]_D^{20} = +304$ ($c = 0.05$ in THF); IR (KBr): $\tilde{\nu} = \nu(C{\equiv}C)$ 2091, $\nu(C{=}O)$ 1713, $\nu(C{=}N)$ 1600 cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 164.47$ (br, COO), 161.23 (br, N=C), 150.37 (br, Ar), 129.93 (br, Ar), 127.95 (br, Ar), 117.80 (br, Ar), 88.53 (br, CH), 68.83 (br, Cp), 68.60 (br, Cp), 67.92 (br, Cp), 66.11 (br, Cp), 20.50 ppm (br, CH_3). Elemental analysis (%) calcd for $C_{2026}H_{1760}N_{100}Cl_2Fe_{100}O_{200}P_4PdPt$: C 66.14, H 4.82, N 3.81; Found: C 65.69, H 5.29, N 3.74.

(*R*)-**3b**: Similar reaction to that with (*R*)-**2a** but using monomer (*R*)-**2b** gave (*R*)-**3b** as a yellow solid in 90% yield. $[\alpha]_D^{20} = +140$ ($c = 0.05$ in THF); IR (KBr): $\tilde{\nu} = \nu(C\equiv C)$ 2095, $\nu(C{=}O)$ 1714, $\nu(C{=}N)$ 1601 cm^{-1}; ^{13}C NMR(100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 164.60$ (br, COO), 162.07 (br, N=C), 150.78 (br, Ar), 130.32 (br, Ar), 126.43 (br, Ar), 113.78 (br, Ar), 89.01 (br, CH), 72.71 (br, Cp), 68.98 (br, Cp), 68.65 (br, Cp), 67.58 (br, Cp), 35.91 (br, CH_2), 31.92 (br, CH_2), 29.74 (br, CH_2), 25.75 (br, CH_2), 22.68 (br, CH_2), 14.11 ppm (br, CH_3 Elemental analysis (%) calcd for $C_{4026}H_{5760}N_{100}Cl_2Fe_{100}O_{200}P_4PdPt$: C 74.57, H 8.95, N 2.16; Found: C 74.49, H 9.10, N 2.19.

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[1] S. Kobayashi, *Catalysis in Precision Polymerization*, Wiley, Chichester, **1997**.

[2] P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515.

[3] For recent papers, see: a) S. Nlate, J. Ruiz, V. Sartor, R. Navarro, J. Blaiz, D. Astruc, *Chem. Eur. J.* **2000**, *6*, 2544; b) R. Resendes, J. A. Massey, K. Temple, L. Cao, K. N. Power-Billard, M. A. Winnik, I. Manners, *Chem. Eur. J.* **2001**, *7*, 2414.

[4] For reviews, see: a) T. Nakano, Y. Okamoto, *Chem. Rev.* **2001**, *101*, 4013; b) J. J. L. M. Cornelissen. A. E. Rowan, R. J. M. Nolte, N. A. J. M. Sommerdijk, *Chem. Rev.* **2001**, *101*, 4039.

[5] a) K. Onitsuka, T. Joh, S. Takahashi, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1179; b) K. Onitsuka, K. Yanai, F. Takei, T. Joh, S. Takahashi, *Organometallics* **1994**, *13*, 3862.

[6] a) F. Takei, K. Yanai, K. Onitsuka, S. Takahashi, *Angew. Chem.* **1996**, *108*, 1634; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1554; b) F. Takei, K. Yanai, K. Onitsuka, S. Takahashi, *Chem. Eur. J.* **2000**, *6*, 983.

[7] a) M. Muller, R. Zentel, *Macromolecules* **1996**, *29*, 1609; b) S. Mayer, G. Maxein, R. Zentel, *Macromolecules* **1998**, *31*, 8522; c) K. Maeda, Y. Okamoto, *Macromolecules* **1999**, *32*, 974.

[8] a) A. Ueno, K. Takahashi, J. Anzai, T. Osa, *J. Am. Chem. Soc.* **1981**, *103*, 6410; b) O. Pieroni, A. Fissi, N. Angelini, F. Lenci, *Acc. Chem. Res.* **2001**, *34*, 9.

[9] a) L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, A. Altomare, C. Carlini, R. Solaro, *Polymer* **1998**, *39*, 6621; b) L. Angiolini, R. Bozio, L. Giorgini, D. Pedron, G. Turco, A. Dauru, *Chem. Eur. J.* **2002**, *8*, 4241.

[10] M. Fujiki, *J. Am. Chem. Soc.* **2000**, *122*, 3336.

[11] a) E. Yashima, K. Maeda, Y. Okamoto, *Nature* **1999**, *399*, 449; b) K. Maeda, E. Yashima, *Yuki Gosei Kagaku Kyokaishi* **2002**, *60*, 878.

[12] For the synthesis of chiral ferrocenyl alcohol, see: a) J. Wright, L. Frambes, P. Reeves, *J. Organomet. Chem.* **1994**, *476*, 215; b) L. Schwink, P. Knochel, *Tetrahedron Lett.* **1996**, *37*, 25.

[13] Chiral ferrocenyl isocyanide (*R*)-**2** was prepared from (*R*)-1-ferrocenyl alcohol[12] by the literature method.[6] (*R*)-**2a**: Yellow solid, $[\alpha]_D^{20} = -75$ ($c = 0.05$ in THF); MS(EI): m/z 359 [M^+]; ^1H NMR(400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.08$ (d, $J = 8.5$ Hz, 2H; Ar), 7.43 (d, $J = 8.5$ Hz, 2H; Ar), 6.08 (q, $J = 6.3$ Hz, 1H; CH), 4.33–4.28 (m, 2H; Cp), 4.20–4.18 (m, 2H; Cp), 4.16 (s, 5H; Cp), 1.69 ppm (d, $J = 6.3$ Hz, 3H; CH_3). (*R*)-**2b**: Yellow solid, $[\alpha]_D^{20} = -42$ ($c = 0.05$ in THF); MS(FAB): m/z 639 [M^+]; ^1H NMR(400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.13$ (d, $J = 8.3$ Hz, 2H; Ar), 7.46 (d, $J = 8.3$ Hz, 2H; Ar), 6.00 (t, $J = 6.8$ Hz, 1H; CH), 4.33–4.22 (m, 2H; Cp), 4.17–4.15 (m, 2H; Cp), 4.11 (s, 5H; Cp), 1.95 (dt, $J = 6.8$ Hz, $J = 6.8$ Hz, 2H; CH_2), 1.27–1.22 (m, 38H; $C_{19}H_{38}$), 0.88 ppm (t, $J = 6.8$ Hz, 3H; CH_3).

[14] F. Takei, H. Hayashi, K. Onitsuka, N. Kobayashi, S. Takahashi, *Angew. Chem.* **2001**, *113*, 4216; *Angew. Chem. Int. Ed.* **2001**, *40*, 4092.

[15] a) I. Cuadrado, C. M. Casado, B. Alonso, M. Moran, J. Losada, V. Belsky, *J. Am. Chem. Soc.* **1997**, *119*, 7613; b) K.-W. Poon, Y. Yan, X.-Y. Li, D. K. P. Ng, *Organometallics* **1999**, *18*, 3528.

[16] Electrolytic redox reactions of **3b** were performed in a CH_2Cl_2 solution containing 0.1 mol dm^{-3} of $[NBu_4][PF_6]$ under potentiostatic conditions at 1.0 V (oxidation) and 0.2 V (reduction) versus Ag/AgCl. A platinum mesh was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively.

[17] F. G. Herring, R. A. N. McLean, *Inorg. Chem.* **1972**, *11*, 1667.